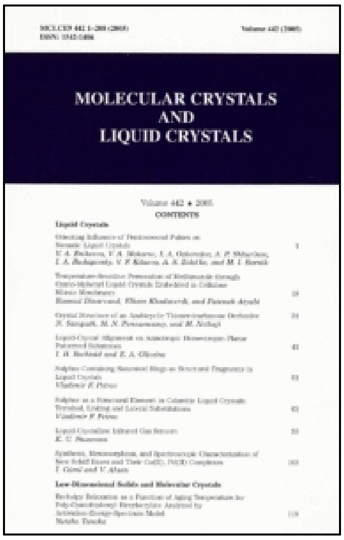


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644168

Preparation of Crosslinked Liquid-Crystalline Polymers by Electron-Beam Irradiation and Their Photoinduced Bending Behavior

Yumiko Naka[a]; Jun-ichi Mamiya[a]; Atsushi Shishido[a]; Masakazu Washio[b]; Tomiki Ikeda[a]
[a] Chemical Resources Laboratory, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama, Japan [b] Research Institute for Science and Engineering, Waseda University, Okubo, Shinjyuku-ku, Tokyo, Japan

To cite this Article Naka, Yumiko , Mamiya, Jun-ichi , Shishido, Atsushi , Washio, Masakazu and Ikeda, Tomiki(2010) 'Preparation of Crosslinked Liquid-Crystalline Polymers by Electron-Beam Irradiation and Their Photoinduced Bending Behavior', Molecular Crystals and Liquid Crystals, 529: 1, 71 — 79

To link to this Article: DOI: 10.1080/15421406.2010.495897

URL: http://dx.doi.org/10.1080/15421406.2010.495897

Mol. Cryst. Liq. Cryst., Vol. 529: pp. 71–79, 2010
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2010.495897

Preparation of Crosslinked Liquid-Crystalline Polymers by Electron-Beam Irradiation and Their Photoinduced Bending Behavior

YUMIKO NAKA,[1] JUN-ICHI MAMIYA,[1]
ATSUSHI SHISHIDO,[1] MASAKAZU WASHIO,[2] AND
TOMIKI IKEDA[1]

[1]Chemical Resources Laboratory, Tokyo Institute of Technology,
Nagatsuta, Midori-ku, Yokohama, Japan
[2]Research Institute for Science and Engineering, Waseda University,
Okubo, Shinjyuku-ku, Tokyo, Japan

We proposed a new approach to fabricate bilayer films with a crosslinked azobenzene liquid-crystalline (LC) polymer. The polyethylene (PE) substrates were coated with linear azobenzene LC polymers, and then the azobenzene layers were crosslinked by irradiation with electron beams (EBs). In the EB-irradiated films with ordered azobenzene moieties, exposure to UV light caused trans-cis *isomerization and the change in alignment of azobenzene moieties. Bending of the bilayer films could be induced toward an actinic light source when they were irradiated from the side of the azobenzene layer, while they bent away from the actinic light source upon UV irradiation from the side of the PE layer. In both cases, the bent films reverted to the initial flat state by turning off the light, which could be repeated at room temperature.*

Keywords Azobenzene; electron-beam crosslinking; liquid-crystalline polymer; photoinduced bending

Introduction

Deformations of azobenzene-containing polymers have attracted much attention because the changes of azobenzene moieties taking place at a molecular scale can be converted and/or amplified to a large-scale deformation of polymers. The photoinduced macroscopic deformation of polymers has been observed in photochromic networks above glass-transition temperature (T_g) [1]. In amorphous polymers with azobenzene chromophores at crosslinks, a reversible dilation and contraction of the polymers were reported by Eisenbash [2]. This photomechanical effect is due to the change in configurations of azobenzene moieties upon photoirradiation. Finkelmann *et al.* reported that crosslinked liquid-crystalline (LC) polymers showed

---

Address correspondence to Tomiki Ikeda, Chemical Resources Laboratory, Tokyo Institute of Technology, R1-11, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan. Tel.: +81-45-924-5240; Fax: +81-45-924-5275; E-mail: tikeda@res.titech.ac.jp

contractions up to 20% upon UV irradiation [3]. The reversible deformation of the crosslinked LC polymers, which is induced by the change in alignment of mesogens triggered by photoisomerization of azobenzene mesogens, is much larger than that of amorphous ones. The crosslinked LC polymers having both elasticity of polymer networks and LC properties were prepared by a two-step method [3,4]. In the first step, weak networks are synthesized by a reaction between a polysiloxane and LC monomers end-functionalized by vinyl, acrylate or methacrylate groups. The networks are deformed with constant load to induce network anisotropy, and then fixed by a second reaction. On the other hand, crosslinked LC polymers without polysiloxane main chains could be fabricated by photopolymerization of mixtures of LC monomers and crosslinkers in a glass cell [5–7]. Crosslinked LC polymers composed only of azobenzene mesogens aligned homogeneously bend toward the actinic light source upon UV irradiation [6,7]. In these films, the incident light is absorbed only by the surface region of the films because of a large extinction coefficient of azobenzene moieties in the wavelength region of about 360 nm. Upon exposure to UV light, *trans*-*cis* isomerization of azobenzene mesogens occurs only in the surface region, causing a contraction at the surface of the films. Recently, various three-dimensional movements such as translational and rotational motions have been achieved with laminated films consisting of a crosslinked photoactive polymer aligned homogeneously and a flexible polymer substrate [8,9]. To improve the mechanical properties, a crosslinked polymer film taken off a glass cell was put on the polymer substrate with an adhesive and lamination was performed at an elevated temperature. However, many problems have remained unsolved. For example, the crosslinked polymer films do not have flat and smooth surfaces. Furthermore, when the laminated films are repeatedly irradiated with light, the photoactive layer is peeled off the polymer substrate because of a weak bonding of the interface between the photoactive layer and the polymer substrate.

To overcome these problems, we propose a new approach to fabricate bilayer films with a crosslinked azobenzene LC polymer. The polymer substrates are coated with linear azobenzene LC polymers, and then the azobenzene layers are crosslinked by irradiation with EBs. This approach enables fabrication of large-area films with a thin azobenzene layer, which will lead to the development of high-performance photomobile materials. In this work, we investigated the photoresponsive behavior of the photomobile materials with a thin photoactive layer prepared by the new method.

Experimental

Material

A linear LC polymer with azobenzene mesogens in side chains, **PAz**, was prepared in a Pyrex tube ampoule by atom transfer radical polymerization. Figure 1 shows the chemical structure and the number-average molecular weight (M_n) of **PAz**. After (6-[4-(4-ethoxyphenylazo)phenoxy]hexyl methacrylate (1.0 g, 2.4 mmol), Cu(I)Cl (0.020 g, 0.20 mmol), 1,1,4,7,10,10-hexamethyltriethylenetetramine (54 μL, 0.20 mmol), ethyl-2-bromoisobutyrate (3 μL, 0.02 mmol) and anisole (4.5 mL) were mixed, the mixture was degassed using freeze-pomp-thaw cycles and sealed under vacuum, then stirred for 30 min at room temperature. The azobenzene monomer was synthesized according to a procedure similar to the literature [10]. The reaction

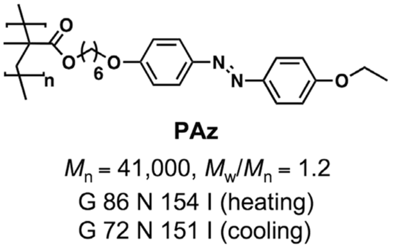
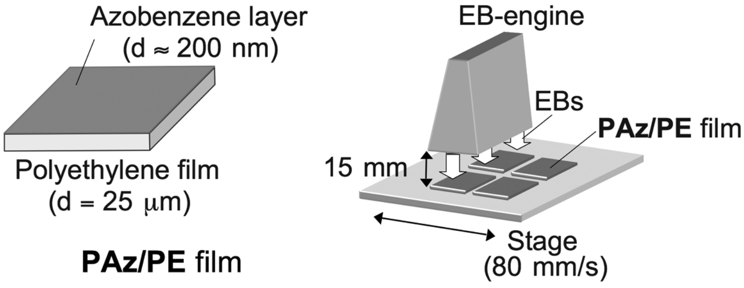


Figure 1. The chemical structure, the number-average molecular weight (M_n) and polydispersity index (M_w/M_n) of an azobenzene LC polymer, **PAz**, used in this study. I, isotropic; N, nematic; G, glassy.

was carried out in a preheated oil bath at 80°C for 2 h 45 min. The polymer solution was passed through a column (silica gel) with tetrahydrofuran (THF) as eluent to remove the catalyst, and the azobenzene polymer was precipitated in a large excess of methanol and finally dried under vacuum. A yellow solid product was obtained. The azobenzene polymer showed the nematic-isotropic phase transition at 154 and 151°C on heating and cooling, respectively (Fig. 5(A)). The glass-transition temperatures (T_gs) of around 80°C were obtained by differential scanning calorimetry (DSC). As a polymer substrate, an unstretched low-density PE film with 25-μm in thickness (Tohcello, T.U.X) was selected because of its high flexibility, good mechanical properties and high reactivity toward EBs.

Preparation of Bilayer Films

The bilayer films (**PAz**/**PE** film) with a **PAz** layer about 200 nm in thickness were prepared by coating PE films with **PAz** cyclohexanone solution with a barcoater (Fig. 2(A)). The film thickness (*d*) was measured with a scanning probe microscope (SHIMADZU, SPM-9500J2) in a tapping mode and UV-vis spectroscopy (JASCO, V-650). The azobenzene moieties in the films were aligned by irradiation with linearly polarized beams at 488 nm (Spectra Physics, Inc., BeamLok2065-7S) at room



(A) (B)

Figure 2. The structure of the bilayer (**PAz**/**PE**) films composed of an azobenzene polymer as a photoactive layer and PE as a flexible substrate (A), and the experimental setup to form crosslinkings in films by EB irradiation (B).

temperature. The films were then irradiated with EBs from the side of the azobenzene layer in a stream of nitrogen gas (Fig. 2(B)).

Characterization

Molecular weight of the polymers was measured by GPC (Japan Spectroscopy, model DG-980-50; column, Shodex GPC 2 × LF804, LF804A; eluent, THF) using standard polystyrenes for calibration. The thermodynamic properties of polymers were analyzed with a DSC (Seiko Instruments Inc., EXTRAR6000, DSC6220) at heating and cooling rates of 10°C/min. At least three scans were performed to check the reproducibility. The mesomorphic properties were examined with a polarizing optical microscope (POM, Olympus. BX50F4) equipped with a hot stage (Mettler, FP-90 and FP-82). The **PAz/PE** films were irradiated with soft-EBs from an EB accelerator (Hamamatsu Photonics, EB-ENGINE®) at room temperature in a stream of nitrogen with a dose rate of 100 kGy/pass (current: 2 mA, pass speed: 80 mm/s). The isomerization of the azobenzene moieties was measured in films by UV-vis spectroscopy upon irradiation with UV light from a UV-LED irradiator (Keyence, UV-400, UV-50H). The optical setup for the evaluation of the photoinduced change in alignment of azobenzene mesogens in films is shown in Figure 8(A). The intensity of a probe beam at 633 nm from a He-Ne laser (NEC, GLS5370) transmitted through a pair of crossed polarizers, with the sample film between them, was measured with a photodiode. The motions of films were recorded by a three-dimensional digital camera (Omron, VC-HRM20Z and VC1000) upon irradiation with UV light.

Results and Discussion

Solubility of EB-Irradiated Polymers

To investigate the formation of crosslinking in both **PAz** and PE, solubility of the polymers was explored after EB irradiation. For exhaustive extraction of the EB-irradiated PE films, the PE film packed into the filter paper thimble was placed in a soxhlet extractor. The PE films extracted with xylene were dried under vacuum for a week, and their weights were measured. The solubility of the EB-irradiated PE films was defined as the ratio of weights of the films after extraction (W_{after}) to that of the films before extraction (W_{before}). The EB-irradiated PE film at 0.5 MGy was insoluble in about 80% as shown in Figure 3(A). Next, we studied the formation of crosslinking in **PAz**. **PAz** dissolves easily in chloroform. The EB-irradiated **PAz/PE** films were stirred in chloroform for 3 days at room temperature. The solubility of **PAz** was defined as the ratio of absorbance at a maximum wavelength (340 nm) of the washed film (A_{washed}) to that of the unwashed film ($A_{unwashed}$). The azobenzene layer on PE films became almost insoluble by irradiation above an EB dose of 2 MGy. Therefore, it was confirmed that **PAz** and PE films were crosslinked by EB irradiation.

Thermal Properties of EB-Irradiated Polymers

Figure 4 shows the DSC thermograms of the **PAz/PE** films irradiated with EBs. The peaks on heating and cooling appeared at around 100°C, corresponding to melting

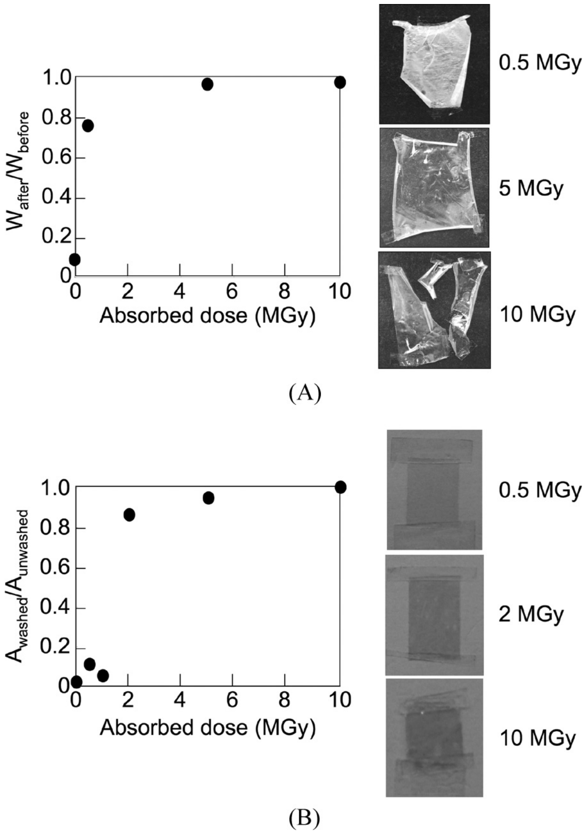


Figure 3. Solubility of PE (A) and azobenzene LC polymer (B) films irradiated with EBs in xylene and chloroform, respectively.

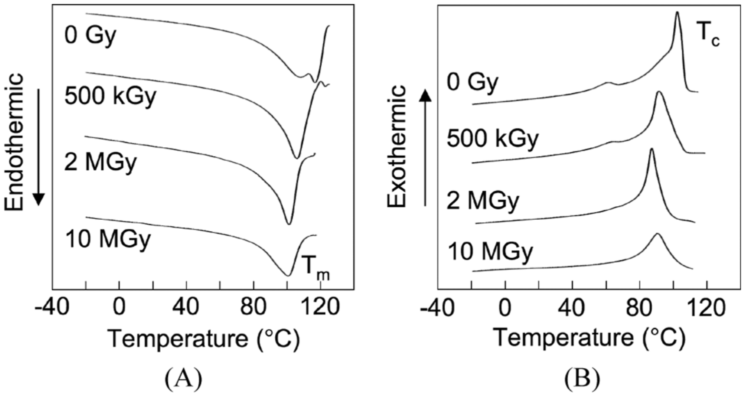


Figure 4. DSC thermograms of the PE films coated with azobenzene LC polymers before and after irradiation with EBs at 10 MGy on heating (A) and cooling (B).

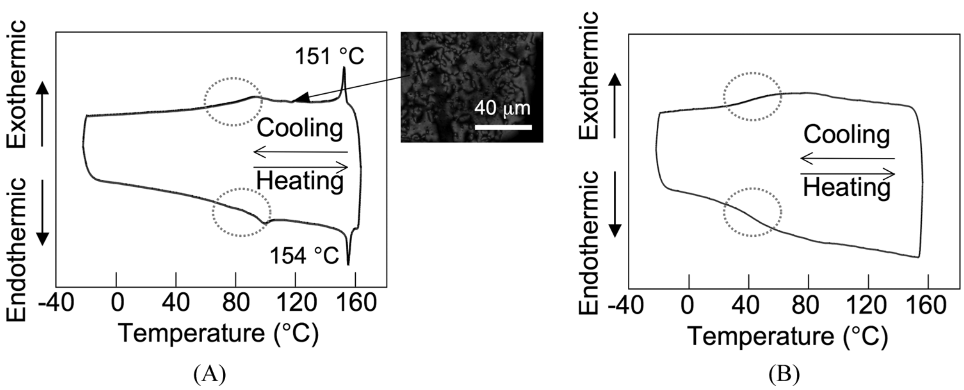


Figure 5. DSC thermograms of azobenzene LC polymers before (A) and after (B) irradiation with EBs at 10 MGy.

(T_m) and crystallization (T_c) temperatures of PE. In the EB-irradiated PE films, the same peaks were obtained. The T_ms, T_cs and their enthalpies decreased with an increase in absorbed doses. Moreover, as shown in Figure 3(A), transparent PE films were obtained by irradiation with EBs above 2 MGy. These results indicate that network formation of the polymer chains occurs by EB irradiation in films, resulting in the lower crystallinity of EB-irradiated PE films as compared with non-EB-irradiated films [11].

In the bilayer film consisting of the azobenzene LC polymer and PE, the T_g of the azobenzene layer could not be detected. We fabricated EB-irradiated azobenzene monolayer films by the following method. NaCl plates were coated with a small portion of **PAz** cyclohexanon solutions by the barcoater method, and then the ordered azobenzene polymer prepared by irradiation with linearly polarized light was irradiated with EBs at 10 MGy. After EB irradiation, the plates were dissolved in water and the resultant EB-irradiated azobenzene polymer films about 1 μm in thickness were dried for 3 days under vacuum at room temperature. As shown in Figure 5, the T_gs of the azobenzene polymers were lowered by EB irradiation: T_g of **PAz** was around 80°C, while that of EB-irradiated **PAz** was around 40°C. In other words, the photoactive layer shows the T_g at around room temperature, which will make it possible to induce bending motions of the bilayer films by photoirradiation without heating.

Order Parameters in EB-Irradiated Films

To evaluate the change in alignment of azobenzene mesogens before and after EB irradiation in the **PAz/PE** films, the polarized absorption spectra were measured. $A_{\|}$ and $A_{\perp}$ are absorbance parallel and perpendicular to the alignment direction of azobenzene mesogens before EB irradiation, respectively. The order parameter (S) was estimated from $A_{\perp}$ and $A_{\|}$ by Eq. (1).

$$S = \frac{A_{\perp} - A_{\|}}{A_{\perp} + 2A_{\|}} \tag{1}$$

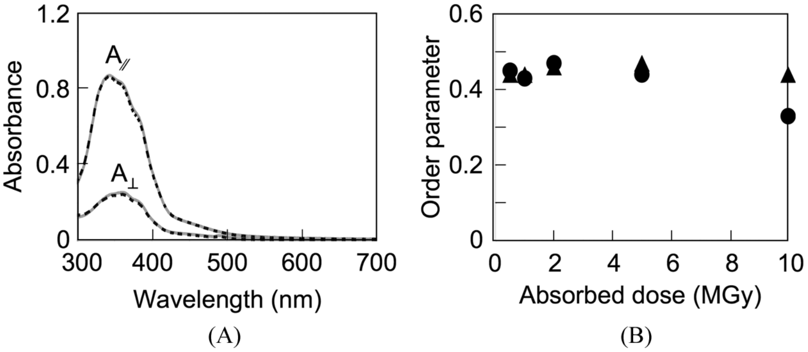


Figure 6. Polarized absorption spectra of the azobenzene LC polymers in films before (solid line) and after (broken line) irradiation with EBs at 2 MGy (A). $A_{\|}$ and $A_{\perp}$ are absorbance parallel and perpendicular to the alignment direction of the azobenzene mesogens, respectively. Order parameter of the azobenzene mesogens in films before (triangles) and after (circles) EB irradiation at various absorbed dose (B).

The bilayer films with an azobenzene layer aligned homogeneously could be prepared upon irradiation with linearly polarized light, in which the values of S was about 0.4. As shown in Figure 6(A), almost the same spectra of the films were obtained before and after EB irradiation. As a result, the order of alignment of azobenzene mesogens was maintained after EB irradiation as shown in Figure 6(B).

Photoisomerizaiton and Photoinduced Change in Alignment of Azobenzene Mesogens in EB-Irradiated Films

To study the photoresponsive behavior of the EB-irradiated films, we prepared a sample composed of an EB-irradiated azobenzene polymer as a photoactive layer and a quartz glass plate as a hard and transparent substrate, whose color remained unchanged after EB irradiation. UV–vis spectra were measured in the EB-irradiated films at 10 MGy as shown in Figure 7. Upon irradiation at 365 nm, the band at

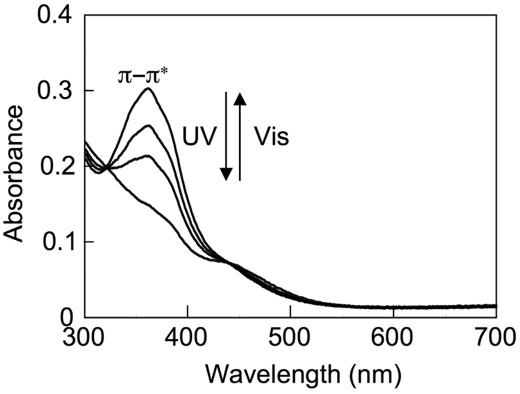


Figure 7. A change in UV-vis absorption spectra of the EB-irradiated film at 10 MGy by irradiation with UV (365 nm, 50 mW/cm^2) and visible (530 nm, 5 mW/cm^2) light.

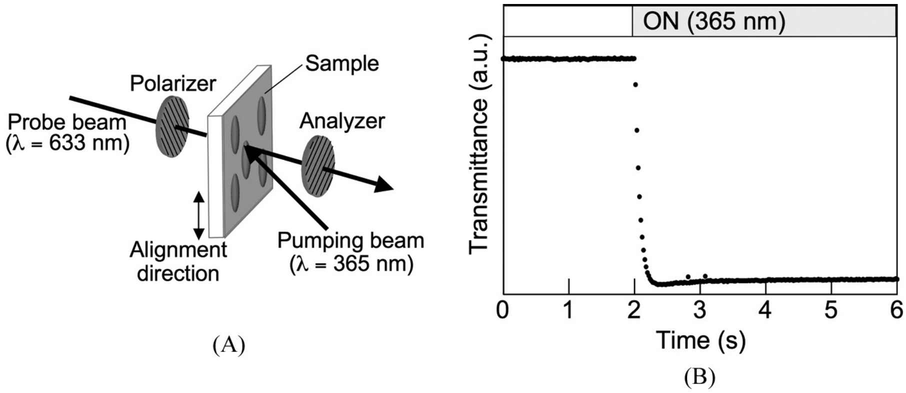


Figure 8. Optical setup around the sample for the evaluation of the change in transmittance upon irradiation with UV light (A). A change in transmittance of an ordered azobenzene polymer film irradiated with EBs at 10 MGy upon exposure to UV light (365 nm, 50 mW/cm^2).

360 nm owing to the π-π^* transition of azobenzene chromophores decreased, indicating the typical photoisomerization behavior of azobenzene moieties. It was found that *trans*-*cis* photoisomerization of azobenzene moieties was induced even after EB irradiation.

To explore the change in alignment of azobenzene moieties, the EB-irradiated films were placed between a pair of crossed polarizers and transmittance was monitored upon irradiation with UV light at 365 nm. The transmittance decayed immediately and finally reached to a constant value upon exposure to UV light as shown in Figure 8. This means that the order of alignment of azobenzene mesogens is reduced

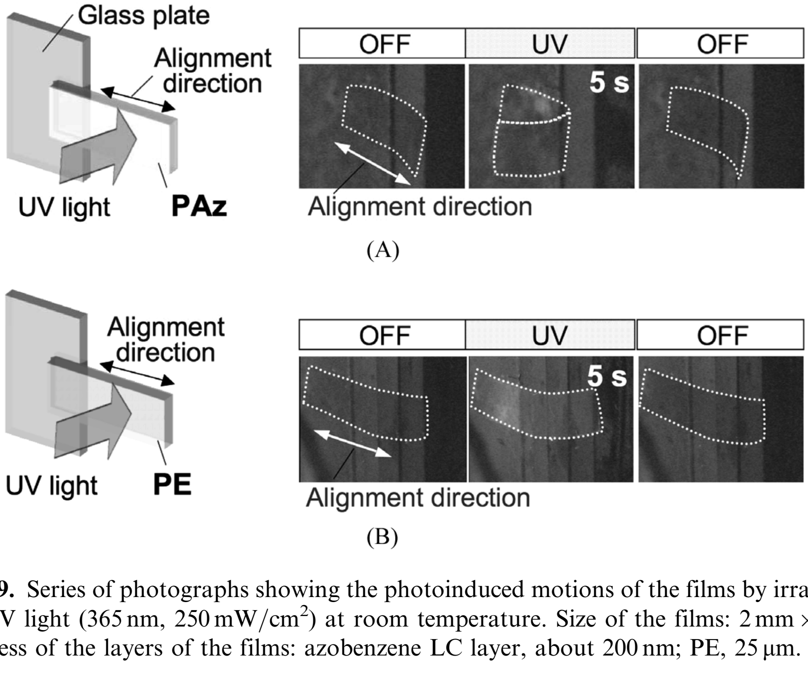


Figure 9. Series of photographs showing the photoinduced motions of the films by irradiation with UV light (365 nm, 250 mW/cm^2) at room temperature. Size of the films: 2 mm × 5 mm. Thickness of the layers of the films: azobenzene LC layer, about 200 nm; PE, 25 μm.

upon UV irradiation. However, the transmittance did not reach zero by continues irradiation with UV light, presumably because the LC-isotropic phase transition is suppressed by the formation of crosslinking in the azobenzene layer.

Photoinduced Motion of EB-Irradiated Films

The photoinduced motions of the EB-irradiated bilayer films were investigated by irradiation with UV light at room temperature. Part of a film was pasted to a glass plate and irradiated with unpolarized light as shown in Figure 9. Exposure to UV light little induced bending motion of non-EB-irradiated bilayer films. On the other hand, the EB-irradiated bilayer film bent toward the actinic light source by irradiation with UV light from the side of azobenzene layer, and the bent film reverted to the initial flat state by turning off the light, which could be repeated at room temperature (Fig. 9(A)). When these films were irradiated with UV light from the side of the PE layer, the films bent away from the actinic light source (Fig. 9(B)).

Conclusions

The bilayer films consisting of azobenzene liquid-crystalline (LC) polymers (**PAz**) as a photoactive layer and polyethylene as a flexible substrate were crosslinked by irradiation with electron beams (EBs) at room temperature. The glass-transition temperatures (T_gs) of **PAz** decreased to around room temperature by EB irradiation. In EB-irradiated films, the azobenzene moieties still showed reversible *trans*-*cis* photoisomerization. The order of alignment of azobenzene mesogens was reduced by irradiation with UV light in EB-irradiated films. Moreover, the bending motions of the bilayer films with thin azobenzene polymer layer prepared upon EB irradiation could be induced by irradiation with UV light.

References

[1] Ikeda, T., Mamiya, J., & Yu, Y. (2007). *Angew. Chem. Int. Ed.*, *46*, 506.
[2] Eisenbach, C. D. (1980). *Polymer*, *21*, 1175.
[3] Finkelmann, H., Nishikawa, E., Pereira, G. G., & Warner, M. (2001). *Phys. Rev. Lett.*, *87*, 015501.
[4] Küpfer, J., & Finkelmann, H. (1991). *Makromol. Chem. Rapid Commun.*, *12*, 717.
[5] Broer, D. J., Finkelmann, H., & Kondo, K. (1988). *Makromol. Chem.*, *189*, 185.
[6] Ikeda, T., Nakano, M., Yu, Y., Tsutsumi, O., & Kanazawa, A. (2003). *Adv. Mater.*, *15*, 201.
[7] Kondo, M., Yu, Y., & Ikeda, T. (2006). *Angew. Chem. Int. Ed.*, *45*, 1378.
[8] Yamada, M., Kondo, M., Mamiya, J., Yu, Y., Kinoshita, M., Barrett, C. J., & Ikeda, T. (2008). *Angew. Chem. Int. Ed.*, *47*, 4986.
[9] Yamada, M., Kondo, M., Miyasato, R., Naka, Y., Mamiya, J., Kinoshita, M., Shishido, A., Yu, Y., Barrett, C. J., & Ikeda, T. (2009). *J. Mater. Chem.*, *19*, 60.
[10] Angeloni, A. S., Caretti, D., Carlini, C., Chiellini, E., Galli, G., Altomare, A., Solaro, R., & Laus, M. (1989). *Liq. Cryst.*, *4*, 513.
[11] Oshima, A., Nagai, H., Muto, F., Miura, T., & Washio, M. (2006). *J. Photopolym. Sci. Tech.*, *19*, 123.